THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)

(54) Title: RADIATION CURABLE RESINS COMPRISING HYPERBRANCHED POLYESTERS

(57) Abstract

Hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups, each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride, and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups. Further in the hyperbranched polyester (meth)acrylic anhydride and/or an aliphatic carboxylic anhydride form ester linkages with the free hydroxyl groups. The invention also comprises a process for the production of hyperbranched polyesters and such polyesters obtainable by the process. The hyperbranched polyesters can be used as resins, curable by UV irradiation, for the production of coatings, adhesives, laminates, foils and thin films and fibre-reinforced composites.

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|---|---|---|---|---|---|
| AT | Austria | GB | United Kingdom | MR | Mauritania |
| AU | Australia | GE | Georgia | MW | Malawi |
| BB | Barbados | GN | Guinea | NE | Niger |
| BE | Belgium | GR | Greece | NL | Netherlands |
| BF | Burkina Faso | HU | Hungary | NO | Norway |
| BG | Bulgaria | IE | Ireland | NZ | New Zealand |
| BJ | Benin | IT | Italy | PL | Poland |
| BR | Brazil | JP | Japan | PT | Portugal |
| BY | Belarus | KE | Kenya | RO | Romania |
| CA | Canada | KG | Kyrgystan | RU | Russian Federation |
| CF | Central African Republic | KP | Democratic People's Republic | SD | Sudan |
| CG | Congo | | of Korea | SE | Sweden |
| CH | Switzerland | KR | Republic of Korea | SI | Slovenia |
| CI | Côte d'Ivoire | KZ | Kazakhstan | SK | Slovakia |
| CM | Cameroon | LI | Liechtenstein | SN | Senegal |
| CN | China | LK | Sri Lanka | TD | Chad |
| CS | Czechoslovakia | LU | Luxembourg | TG | Togo |
| CZ | Czech Republic | LV | Latvia | TJ | Tajikistan |
| DE | Germany | MC | Monaco | TT | Trinidad and Tobago |
| DK | Denmark | MD | Republic of Moldova | UA | Ukraine |
| ES | Spain | MG | Madagascar | US | United States of America |
| FI | Finland | ML | Mali | UZ | Uzbekistan |
| FR | France | MN | Mongolia | VN | Viet Nam |
| GA | Gabon | | | | |

1
Radiation curable resins comprising hyperbranched polyesters

The present invention relates to new hyperbranched
polyesters and a process for the production thereof and
curable resins comprising the polyesters.

5        Radiation-curable resins are increasingly used in
various industrial applications, replacing conventional
thermally cured and solvent based coatings and adhesives. The
radiation-curable resins have favourable properties, e.g.,
high speed and low energy consumption of cure, solvent-free
10   formulations, room temperature operation and high quality
end-products. The principal components of a radiation-curable
resin are oligomers (or prepolymers) and comonomers. The
oligomers constitute the backbone of the three-dimensional
polymer network formed by curing. Important types of oligo-
15   mers commonly used for coating are acrylated epoxies, acryla-
ted polyurethanes, unsaturated polyesters and acrylated
polyesters (or polyethers) which give desired properties of
the final cured films. However, those oligomers usually
consist of linear molecular chains. The viscosity of the
20   resin increases rapidly with increasing chain length of the
oligomer. To obtain an operational viscosity of the formula
for spraying, dipping, roll coating, etc., large amounts of
multifunctional comonomer are required for the primary func-
tion of viscosity control. In addition, the comonomers have
25   important effects on the cure reaction and the properties of
the final product. Some of the comonomers have low cure rate,
cause shrinkage of the film during curing, and have high
costs and a limited shelf life. Multifunctional acrylates are
the preferred monomers in radiation-curable systems because
30   of their rapid curing rates and low prices. The common
acrylate monomers are volatile and toxic, and have strong
odour. Therefore, the trend is to use radiation-curable
oligomers with viscosity close to the required application
viscosity in order to reduce or eliminate the use of comono-
35   mers.

An object of the present invention therefore was to
obtain oligomers with reduced viscosity compared to known

**CONFIRMATION
COPY**

oligomers with similar molecular weight.

A further object of the invention was to present
oligomers which in resin applications needs a lower amount of
multifunctional comonomers or none at all, while the resins
5   still have a low viscosity, a high cure rate, an acceptable
degree of curing and the final products have good mechanical
properties.

A further object of the invention was to offer a
process for the production of such oligomers.

10  The objects of the invention was solved by the
hyperbranched polyester, the process for the production of
these hyperbranched polyesters and resin comprising them, as
claimed in the claims.

Oligomers with a strongly branched structure are a
15  new family of polymers which has been attracting increasing
interest for many applications, e.g., in agriculture, medi-
cine, cosmetics, adhesives and coatings. The oligomers are
referred to as hyperbranched polyesters with a three-dimen-
sional molecular architecture and possessing starburst
20  topology (D.A. O'Sullivan, Chem. Eng. News, 20 (1993); D.A.
Tomalia, A.M. Naylor, and W.A. Goddard III, Angew.Chem. Int.
Ed.Engl., 29, 138 (1990). An important structural difference
between linear oligomers and hyperbranched polyesters is that
a linear oligomer of sufficient molecular weight contains an
25  entanglement of flexible molecular chains, while a hyperbran-
ched polyester is a compact molecule with many branches which
carry a high number of terminal functional groups on each
molecule.

With the present invention it was found that hyper-
30  branched polyesters with reactive acrylate double bonds at
chain extremities can be used to reduce viscosity, increase
reaction rate, and improve adhesion to substrates due to
their very special molecular structures. This new kind of
molecules modifies the physical and chemical properties both
35  of the resin system and of the final product after curing,
thereby facilitating their use in coating and adhesive sys-
tems. Further, with the present invention hyperbranched

polyesters with high molecular weight can be obtained in a simple process from readily available and inexpensive raw materials.

Hyperbranched polyester research is still fairly new, and to date no commercial products are available. The main difficulties in preparing three-dimensional and ordered hyperbranched polyesters are preserving the regularity and order in the structures, characterization of the products, and separating the products from the excess of reactants. Little work has been performed to prepare adhesive and coating systems with hyperbranched polyesters, especially for radiation curing applications. A series of work on allyl ether maleate hyperbranched polyesters for UV curing coatings have been reported (M.Johansson, E. Malmström, and A.Hult, J.Polym.Sci., Part A: Polym.Chem., 31, 619 (1993); E.Malmström and A.Hult "Hyperbranched polyesters and their Degree of Branching as Determined by $^{13}$C-NMR", Proceedings of Nordic Polymer Days 1994.).

With the present invention it has been possible to synthesize a series of new hyperbranched (meth)acrylated polyesters with different number of terminal double bonds per molecule. The rheological properties of the resins prepared from the polyesters and the mechanical properties of UV cured films are improved in a pronounced manner compared with known polymers.

Thus, the present invention relates to a hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably with 3 carboxyl groups,

each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride,

and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups.

The invention further relates to a hyperbranched

4

polyester as defined above in which (meth)acrylic anhydride
and/or an aliphatic carboxylic anhydride form/s ester link-
ages with the free hydroxyl groups.

5       The present invention further relates to a process
for the production of a hyperbranched polyester, and hyper-
branched polyester obtainable by the process characterized in
that it comprises the following steps:
a) reacting an aromatic polycarboxylic anhydride with 2 to 4
carboxyl groups, preferably 3 carboxyl groups, with a polyol
10      with 3 to 10 reactive hydroxyl groups, preferably of equival-
ent reactivity, in the presence of an activating agent, the
amount of anhydride being at least one mole of anhydride per
hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate
15      or allyl glycidyl ether in an amount at least corresponding
to one mole of glycidyl (meth)acrylate or allyl glycidyl
ether per free carboxylic acid group of the product of a).
The process and the polyester obtainable by the process can
further comprise the following step:
20      c) the product from step b) is further reacted with (meth)-
acrylic anhydride in an amount sufficient to esterify a part
or all of the free hydroxyl groups of the product from step
b). The products from step b) or c) can further be reacted
with an aliphatic carboxylic anhydride in an amount to
25      esterify a part of or all of the remaining hydroxyl groups of
the products.

        Two principally different methods have been devel-
oped for the synthesis of hyperbranched polymers: a conver-
gent growth approach, where growth begins at the chain ends,
30      and a divergent growth approach, where growth begins at a
central core. In the present invention, the hyperbranched
polyesters with terminal double bonds were synthesized by
controlled stepwise divergent preparation, i.e., the syn-
thesis started at the centre of the hyperbranched polyester.
35      Two or three steps were needed to obtain hyperbranched
polyesters with a predetermined number of terminal double
bonds located at the surface of the oligomeric sphere. The

reaction scheme for the synthesis of the hyperbranched
polyester can be illustrated for a polyol with 4 hydroxyl
groups as shown in Figure 1 (B is hydroxyl groups, and D is
unsaturated groups). New nomenclature developed by K. L.
5    Wooley, J. M. J. Fréchet and C. J. Hawker, Polymer vol. 35,
No. 21, 1994, names the starburst hyperbranched molecule of
Figure 1 a dendritic polymer.

In the first reaction step an aromatic carboxylic
anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl
10   groups, and a polyol with 3 to 10 hydroxyl groups and an
activating agent were heated to temperatures about or below
100°C, preferably initially to 70 to 80°C and gradually
increasing to about 100°C at the end of the reaction, in the
presence of a solvent and under inert gas atmosphere, prefer-
15   ably nitrogen atmosphere. The aromatic carboxylic anhydride
is most preferably 1,2,4-benzenetricarboxylic anhydride.
Suitable polyols are all polyols having 3 to 10 hydroxyl
groups and the hydroxyl groups are preferably of equivalent
reactivity, which means that the esterification of each
20   hydroxyl group will proceed equally easy to start the build-
ing up of the regular molecule. Examples of such polyols are
trimethylolpropane, pentaerythritol or a dimer thereof, mono-
and disaccharides, with pentaerythritol as a preferred embod-
iment. The amount of added anhydride is at least one mole of
25   anhydride per hydroxyl group of the polyol, but preferably
the anhydride is added in an excess amount. An excess of 20 -
50 mol % is suitable. An activating agent is used to activate
the anhydride group. The activating agent is present in a
catalytic amount. As activating agent stannous chloride is a
30   preferred embodiment. A suitable solvent is for example N,N-
dimethylformamide (DMF).

For a product mixture of 1,2,4-benzenetricarboxylic
anhydride with pentaerythritol the IR spectrum with residual
1,2,4-benzenetricarboxylic anhydride is shown by curve 1 in
35   Figure 2. Toluene was used to wash the reaction product to
remove the excess of 1,2,4-benzenetricarboxylic anhydride
until no peaks at 1760 and 1850 cm$^{-1}$ for anhydride groups

could be observed, shown as curve 2 in Figure 2. The wide
absorption bands at the range of 2750 to 3400 cm$^{-1}$ in the IR
spectrum indicate the terminal carboxyl groups on the benzene
ring. For this product mixture each polyolester of the poly-
5    carboxylic acid anhydride has two carboxyl end groups. Three
isomer products could be obtained in this system, and the
molecular structures are shown in Figure 3. The product is
largely a mixture of meta and para isomers of the ester
according to the relative reactivity of the anhydride and the
10   carboxyl groups at low reaction temperature. A small amount
of ortho isomer is expected to be a hydrolysis and reesteri-
fication product of para and meta polyolester formed. The
reaction of carboxyl and hydroxyl groups is favoured at
elevated temperatures.

15        The polyolester was further reacted with glycidyl
(meth)acrylate or allyl glycidyl ether in an amount at least
corresponding to one mole of glycidyl (meth)acrylate or allyl
glycidyl ether per free carboxylic acid group of the formed
polyester, preferably in an excess amount, i.e. about 5 wt%.
20   Glycidyl acrylate is the preferred reactant. The reaction is
carried out in a solvent, such as a mixture of DMF and
toluene in the presences of a basic catalyst and an inhibitor
for radical polymerization until no carboxyl groups could be
detected by end-group titration. As basic catalysts common
25   bases can be used, but benzyl dimethyl amine is preferred.
Conventional inhibitors such as hydroquinone is used. The
reaction temperature is below 100°C, preferably about 70°C.
The IR spectrum of the product is shown as curve 3 in Figure
2. The appearance of the wide absorption at around 3460 cm$^{-1}$
30   means the formation of hydroxyl groups on the molecular
chains due to reaction of epoxy and carboxyl groups. Finally,
residual solvent was removed by evacuation at low tempera-
ture. The final "starburst" hyperbranched polyester products
with double bonds at the end groups are translucent viscous
35   liquids with one hydroxyl group at each end group. The mol-
ecular structure, when started with pentaerythritol, is
ideally sphere-like, with about 8 end-double bonds. The

principal formula is shown in Figure 4.

The hydroxyl groups of the hyperbranched polyester with terminal double bonds were reacted further by ester formation with (meth)acrylic anhydride in an amount suffi-
5  cient to esterify a part of or all of the free hydroxyl groups in order to prepare the hyperbranched polyester molecules with further end-double bonds. Of the two acrylic anhydrides, the methacrylic anhydride is preferred. The hyperbranched polyester started from pentaerythritol with
10  about 16 end-double bonds with the idealized formula is shown in Figure 5. The IR spectrum of the hyperbranched polyester with about 16 double bonds is shown by curve 4 in Figure 2. Almost no peak for hydroxyl group could be observed.

In a last step the product with end-double bonds is
15  reacted with an aliphatic carboxylic anhydride, preferably acetic anhydride to esterify a part of or all of the remaining hydroxyl groups on the molecular chains for decreasing molecular polarity of the hyperbranched polyester, and improving its compatibility with multifunctional comonomers.
20  This esterification can also be made of the hydroxyl groups of the hyperbranched polyester before the previous reaction with (meth)acrylic anhydride, thus omitting the further introduction of (meth)acrylic double bonds. The final hyperbranched polyester products with terminal double bonds after
25  modifying, prepared in the present invention are fairly transparent colourless viscous liquids. As shown in Figure 4 and 5 the double bonds are in end groups, located at the surface of the oligomeric sphere, which is highly favourable for UV cure.
30  The polydispersity measured by GPC analysis (Figure 6) varied from 1,4 to 1,9 at different reactant ratios and reaction temperatures with molecular weights of maximum 2500 obtained, which corresponds to a modified polyester molecule with four main branches. The wide molecular weight distribu-
35  tion is mainly attributed to incomplete reaction between 1,2,4-benzenetricarboxylic anhydride and pentaerythritol, hyperbranched polyester fragmentation during hyperbranched

8

polyester growth, and to the small excess of glycidyl
(meth)acrylate monomer which react further with by-products
in the system, responsive to UV irradiation.

The hyperbranched polyester according to the inven-
tion can be used as curable resins. The resins are preferably
cured by UV or EB radiation and most preferably by UV radi-
ation. The resins have lower viscosity than known oligomer
resins and can be used without a comonomer or with lower
amounts of comonomer than for conventional oligomer resins.
The UV curing of the resin according to the invention is very
rapid, down to parts of a second at room temperatur oper-
ation. This means a high speed of cure and low energi con-
sumption. The obtained products have a high glass transition
temperature, resulting in products of high hardness, for
example coatings or laminates with high surface hardness.

The resins are solvent free and can be prepared
from 100 % of the hyperbranched polyester according to the
invention. The resins can however, also comprise multifunc-
tional monomers. A suitable amount of comonomer is 5 - 20 wt
% and the rest 80 - 95 wt % being the hyberbranched
polyester. The resins preferably comprise a photofragmenting
initiator. The amount of photofragmenting initiator used is
in the range 1 - 5 wt % based on the resin. Conventional
photofragmenting initiators can be used and a preferred
initiator is benzoyl dimethylketol. As multifunctional mono-
mers compounds with reactive double bonds can be used, such
as trimethylolpropane tri(meth)acrylate, hexandiol diacryla-
te, trimethylolpropane triallylether, pentaerythritol tri/te-
tra-allylether, triallylcyanurate, trimethylolpropane tri-
acrylether, pentaerythritol tetraacrylether. Trimethylolpro-
pane triacrylate being a preferred embodiment.

The resin according to the invention can be used in
many different fields of which could be mentioned coatings,
adhesives, laminates, foils and thin films and fibre-rein-
forced composites.

The invention will now be illustrated with
the following examples which however, are not intended to

9

restrict the invention. With parts and per cent are meant
parts per weight and weight-%, if nothing else is mentioned.

The following chemicals are used:

5    Pentaerythritol [PETL]

1,2,4-Benzenetricarboxylic Anhydride [BTCA]

Glycidyl Acrylate [GA]

Methacrylic Anhydride [MAA]

Acetic Anhydride [AA]

10   Stannous Chloride [SC]

Benzyldimethylamine [BDMA]

Hydroquinone [HQ]

Dimethyl Formamide [DMF]

Trimethylolpropane Triacrylate (TMPTA)

15   Benzoyldimethylketol (BDK)

Example 1

92,2 g (0.48 mol) BTCA is dissolved in 100 ml DMF
at 80°C. 10.9 g (0.08 mol) PETL and 0.1 g (0.1 wt%) SC are
20   added, and the solution is kept at 80°C for 8 hours, and then
heated to 100°C for 10 hours under $N_2$. Most of DMF is
distilled off in vacuum and toluene is poured into the prod-
uct to dissolve the residual BTCA. The product is washed with
toluene until no BTCA is detected in IR spectra (1760 and
25   1850 cm$^{-1}$ for anhydride groups). 57.2 g polyolester is
obtained, as a white powder, with the yield of about 79 %
after completely removing the solvents. The acid number of
475 mg KOH/g polyester is determined by titration with 0.1 N
KOH. 65.09 g (0.508 mol with a 5 % excess) GA is added slowly
30   drop by drop at 70°C together with 5 g (2.5 %) BDMA as cata-
lyst and 1000 ppm HQ as inhibitor, dissolved in 70 ml DMF.
After 7 hours at 70°C no carboxyl groups can be detected by
titration. DMF is distilled off in vacuum. The product is a
viscous liquid with maximum 8 acrylate and 8 hydroxyl groups
35   per molecule. This product is called D-1OH.

12.4 g (0.121 mol) AA is added to 40.8 g D-1OH in
50 ml DMF which reacts with about 6 hydroxyl groups per

molecule (averaged about 2 OH groups per molecule remain).
The product solution is then heated for 2 hours at 70°C and
DMF is distilled off in vacuum. The obtained product, called
D-1, is a viscous liquid with about 8 acrylate groups and 2
5      hydroxyl groups per molecule.


Example 2
        40.8 g D-1OH is dissolved in 50 ml DMF with 500 ppm
HQ and 12.4 g (0.08 mol) MAA and 4.1 g (0.04 mol) AA are
10     added slowly, drop by drop at 70°C for two hours to react
with the hydroxyl groups. DMF is removed by vacuum distilla-
tion. The product, called D-2, is a viscous liquid with about
12 (meth)acrylate groups and 2 hydroxyl groups per molecule.


15     Example 3
        40.8 g D-1OH is dissolved in 50 ml DMF with 500 ppm
HQ as inhibitor. 24.8 g MAA (0.161 mol) is added and heated
to 70°C. After 2 hours the reaction is complete. DMF is
removed by vacuum distillation. The product, called D-3, is a
20     viscous liquid with about 8 acrylate and 8 methacrylate
groups per molecule.
        The dynamic viscosity for the products from
Examples 1 to 3 was measured as a function of frequency for
the hyperbranched polyesters with different numbers of double
25     bonds, as shown in Figure 7. The hyperbranched polyester D-1-
OH, according to Example 1, with about 8 double bonds and
without acetic anhydride modification, has the highest vis-
cosity  due to the many hydroxyl groups in the system, resul-
ting in intermolecular hydrogen bonding (hyperbranched
30     polyester aggregation). At decreasing hydroxy functionality,
the dynamic viscosities of the hyperbranched polyester large-
ly decrease in order of D-1, D-2 and D-3, according to
Examples 1 to 3, at lower frequency. D-3 has the lowest
viscosity compared with D-1 and D-2 because of the high
35     number of double bonds (no remaining hydroxyl groups) at the
surface of the spherical molecule. This results in increasing
symmetry of the hyperbranched molecule, apart from less

influence from the hydrogen bonding.

Low viscosity is particularly important in control-
ling the levelling time of a coating and for evaluation of
the processability of a radiation curable coating and adhes-
5      ive. This is especially the case for 100% solid coating
systems for thin films. The oligomer is the principal consti-
tuent and primarily responsible for the basic properties of
the coating. The viscosity of the oligomer is, therefore, an
important parameter since it determines the amount of
10     oligomer required in the final product. For control of the
viscosity of the radiation curable resin there are only two
parameters, namely the viscosity of the oligomer and the
amount of comonomer added.

The principal rheological difference between the
15     branched and the linear polyester molecules lies in the
smaller spatial extension of the branched molecule at a given
molecular mass. The viscosity of the resin is related to the
dynamic extension in space and the segment density within the
volume of the molecule. Therefore, the sphere-like starburst
20     (meth)acrylated polyester according to the invention has
lower viscosity than the linear polyester.

Flow time measurements are another evaluation of
the relative viscosity of various coatings and adhesives,
using a viscosimetric cup. The viscosities of the hyperbran-
25     ched (meth)acrylated polyesters containing 15 wt% tri-
methylolpropane triacrylate (TMPTA), as comonomer and a
conventional epoxy acrylate modified unsaturated polyester
(MUP) containing 35 wt% TMPTA at 21°C are compared in Figure
8. It can be seen that the flow times through the viscosimet-
30     ric cup for hyperbranched polyester resins are much shorter
than for MUP resin. This means that the viscosity of MUP is
much higher than that of hyperbranched polyester. A practical
consequence is that the processability of hyperbranched
polyester containing resins is improved due to lower viscos-
35     ity.

Example 4:

3 parts of BDK were dissolved in 100 parts of a

mixture of 15 % by weight of TMPTA and 85 % by weight of D-1,
D-2 or D-3, the resultant resins were coated on a
polyethylene terephtalate (PET) sheet. The test samples were
cured in air on a conveyer belt with variable speed by UV
5    irradiation for 0,15 seconds under a 300 W/in (120 W/cm)
Model F300 D bulb (Fusion UV Curing Systems) in the exposure
chamber.

### Example 5:

10        The procedure of Example 4 was repeated except that
100 parts of D-1, D-2 or D-3 polyesters are used instead of
the mixture of the polyesters and TMPTA.
          The irradiation time is varied by changing the
speed of the conveyor belt. The polymerization rate of the
15   hyperbranched polyester resins was determined by measuring
the irradiation time required to obtain fully tack-free state
for the cured film using a cotton bar. The data are given in
Figure 9. The resin with oligomer D-3 needs the shortest
curing time to get tack-free state.
20        The glass transition temperatures of the crosslin-
ked (meth)acrylated hyperbranched polyesters D-1, D-2 and D-3
according to Example 5 from Dynamic Mechanical Thermal Analy-
sis (DMTA) measurements are given in Figure 10. It can be
seen that the glass transition temperature increases rapidly
25   with increasing functionality of the cured hyperbranched
oligomer.
          The physical properties of the cured material are
related to the structure of the crosslinked network. The
glass transition temperature, $T_g$, is a function of the flexi-
30   bility of the polymeric chains. If the flexibility decreases,
the transition temperature increases. Flexibility is a func-
tion of chain structure, crosslinked structure and crosslink
density. For the hyperbranched polyesters the spherical shape
of the molecules and the high crosslink density due to its
35   high functionality decreases the flexibility of the cured
films. Therefore, crosslinked hyperbranched polyester give
higher glass transition temperature than crosslinked linear

oligomers as an effect of the structural difference.

The measurements made in the present
invention were performed accordingly:

Molecular Weight Distribution

5          Measurements of molecular weight distribution were
performed on a WATERS 410 GPC system equipped with a WISP 712
automated injector. The columns used were  $\mu$-Styragel of pore
sized: 500, $10^5$, $10^4$, $10^3$, and 100 Ångström with polystyrene
standards for calibration and tetrahydrofuran (THF) as sol-
10   vent.

Dynamic Mechanical Spectroscopy

The dynamic mechanical properties of the hyperbran-
ched polyesters were measured by shear rheometry (Dynamic
Analyser RDAII). Viscous liquid samples were examined at 25°C
15   using two parallel plates of 12.5 mm radius with 0.62 to 0.76
$\mu$m gap over a wide range of frequencies.

Flow Time

Flow time of the resins with multifunctional mono-
mer added was measured using a viscometric cup of number 68
20   for comparison of the viscosity of the hyperbranched
polyesters with that of modified linear unsaturated
polyester.

IR spectra

Infra-red spectra of the polyesters at different
25   reaction stages were recorded on a Perkin-Elmer Model 1710
Fourier Transform Spectrometer prepared as pressed KBr solid
disk or smeared as an acetone solution of the resin on a NaCl
prism to form a thin film.

Thermomechanical analysis

30          Dynamic Mechanical Thermal Analyser (DMTA, Polymer
Laboratories MK II) was used to measure glass transition
temperature ($T_g$) at the range of 40 to 250°C and 1 Hz fre-
quency of completely UV cured films without TMPTA added.

14

## Claims

1. Hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups,
each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride,
and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups.

2. Hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups,
each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride,
and glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups,
and further (meth)acrylic anhydride and/or an aliphatic carboxylic anhydride forming ester linkages with the free hydroxyl groups.

3. Hyperbranched polyester obtainable by a process comprising the following steps:
a) reacting an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups, with a polyol with 3 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, in the presence of an activating agent, the amount of anhydride being at least one mole of anhydride per hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate or allyl glycidyl ether in an amount at least corresponding to one mole of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the product of a).

4. Hyperbranched polyester according to claim 3,

15

characterized in that activating agent is present in a
catalytic amount.

5. Hyperbranched polyester according to claim 3,
characterized in that the activating agent is SnCl$_2$.

6. Hyperbranched polyester obtainable by a process
comprising the steps a) and b) of claim 3 and the further
step:

c) the product from step b) is further reacted with
(meth)acrylic anhydride in an amount sufficient to esterify a
part or all of the free hydroxyl groups of the product from
step b).

7. Hyperbranched polyester obtainable by a process
comprising the steps a) and b) of claim 3 or the steps a), b)
and c) from claim 6 and the further step that the product
from step b) or c) is further reacted with an aliphatic
carboxylic anhydride in an amount to esterify a part of or
all of the remaining hydroxyl groups of the products.

8. Hyperbranched polyester according to claims 2, 6
and 7, characterized in that the (meth)acrylic anhydride and
the aliphatic carboxylic anhydride forming ester linkages
with the free hydroxyl groups is methacrylic anhydride and
acetic anhydride.

9. Hyperbranched polyester according to any of
claims 1 to 8, characterized in that the polyol is
pentaerythritol and the aromatic polycarboxylic anhydride is
1,2,4-benzenetricarboxylic anhydride and the
glycidyl(meth)acrylate is glycidyl acrylate.

10. Hyperbranched polyester according to any of
claims 1 to 9, characterized in that the hyperbranched
polyester is a dendritic polyester or a crosslinked dendritic
polyester.

11. A process for the production of a hyperbranched
polyester, characterized in that it comprises the following
steps:

a) reacting an aromatic polycarboxylic anhydride with 2 to 4
carboxyl groups, preferably 3 carboxyl groups, with a polyol
with 3 to 10 reactive hydroxyl groups, preferably of

equivalent reactivity, in the presence of an activating
agent, the amount of anhydride being at least one mole of
anhydride per hydroxyl group in the polyol,
b) reacting the product from a) with glycidyl (meth)acrylate
or allyl glycidyl ether in an amount at least corresponding
to one mole of glycidyl (meth)acrylate or allyl glycidyl
ether per free carboxylic acid group of the product of a).

    12. A process according to claim 11, characterized
in that the activating agent is present in a catalytic
amount.

    13. A process according to claim 11, characterized
in that the activating agent is SnCl$_2$.

    14. A process according to claim 11, characterized
in that in step a) the reaction mixture is heated to a
temperature below 100°C.

    15. A process according to claim 11, characterized
in that the amount of anhydride in step a) and of acrylate in
step b) are in excess of the stated amount.

    16. A process according to claim 11, characterized
in that the reaction of step b) is made in the presence of a
basic catalyst and an inhibitor for radical polymerization.

    17. A process according to claim 16, characterized
in that the basic catalyst is benzyldimethyldiamine.

    18. A process according to claim 11, characterized
in that it further comprises the following step:
c) the product from step b) is further reacted with
(meth)acrylic anhydride in an amount sufficient to esterify a
part or all of the free hydroxyl groups of the product from
step b).

    19. A process according to claim 18, characterized
in that the anhydride is methacrylic anhydride.

    20. A process according to claims 11 or 18,
characterized in that the product from step b) or c) is
further reacted with an aliphatic carboxylic anhydride in an
amount to esterify a part of or all of the remaining hydroxyl
groups of the products.

    21. A process according to claim 20, characterized

in that the aliphatic carboxylic anhydride is acetic anhydride.

22. A process according to any of claims 11 to 21, characterized in that the polyol is pentaerythritol and the aromatic polycarboxylic anhydride is 1,2,4-benzene-tricarboxylic anhydride and the glycidyl(meth)acrylate is glycidyl acrylate.

23. A process according to any of claims 11 to 22, characterized in that the hyperbranched polyester is a dendritic polyester or a crosslinked dendritic polyester.

24. A curable resin characterized in that it comprises a hyperbranched polyester as defined in any of claims 1 to 10.

25. A curable resin according to claim 24, characterized in that it further comprises a photofragmenting initiator.

26. A curable resin according to claim 24 or 25, characterized in that it comprises a multifunctional monomer.

27. A curable resin according to claim 26 characterized in that the multifunctional monomer is trimethylolpropane triacrylate.

28. A curable resin according to any of claims 24 to 27, characterized in that it is curable with UV irradiation.

29. Use of a curable resin according to any of claims 24 to 28 for the production of coatings, adhesives, laminates, foils and thin films and fibre-reinforced composites.
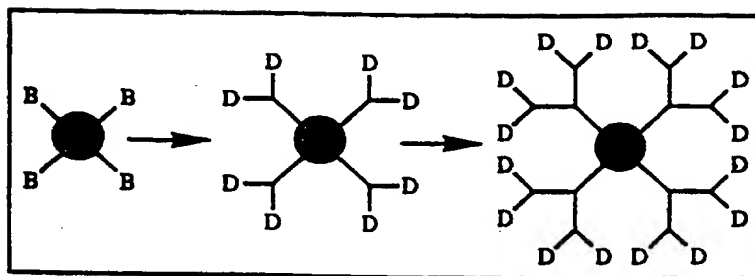
Figure 1  Reaction scheme for the synthesis of the hyperbranched polyester.


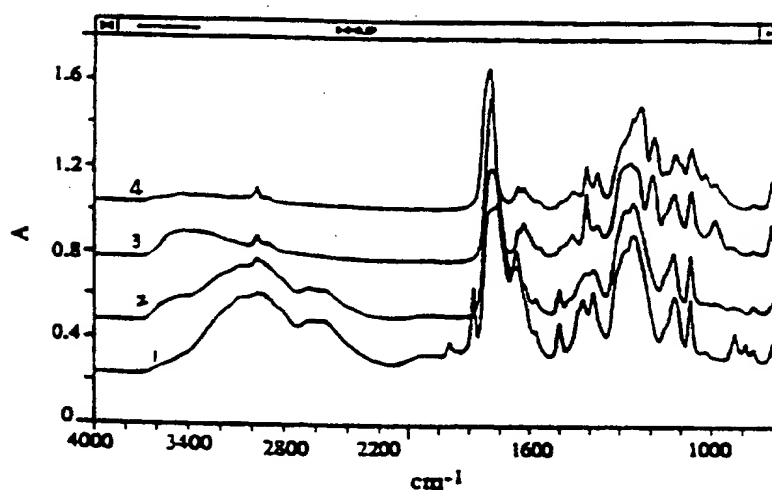
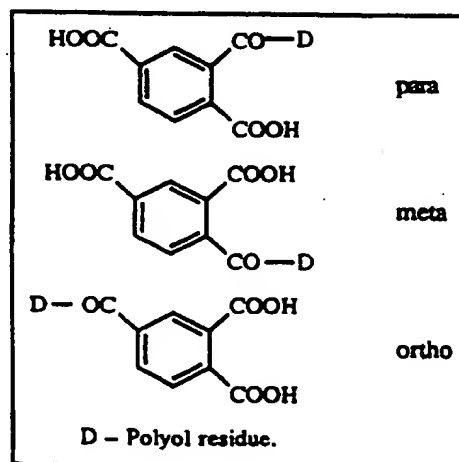Figure 2  IR spectra of the products at different reaction stages.



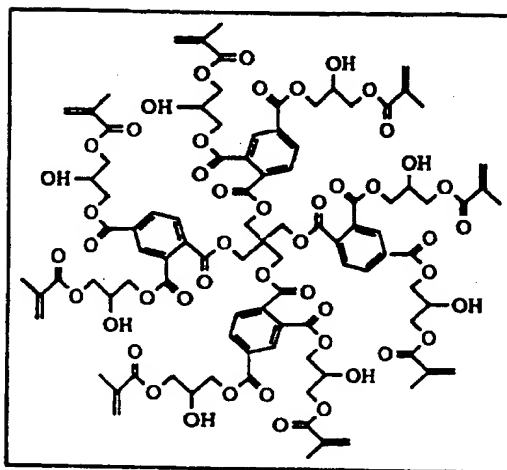Figure 3  Molecular structure of the three polyolester isomers.

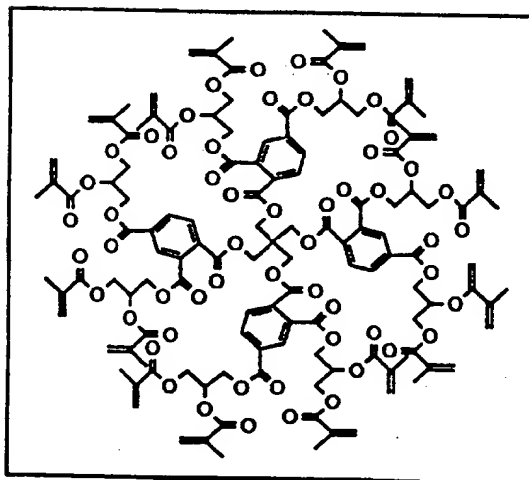Figure 4 Idealized formula of the hyperbranched methacrylated polyester with 8 double bonds.



Figure 5 Idealized formula of the hyperbranched methacrylated polyester with 16 double bonds.
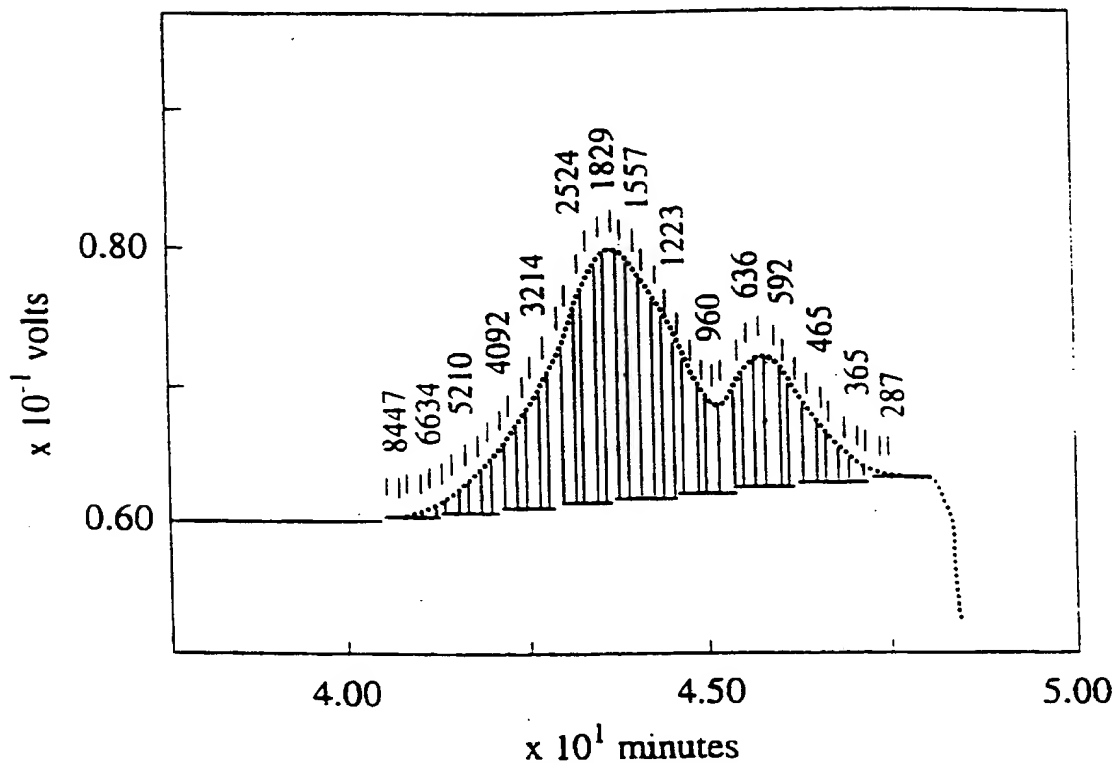
Figure 6   Molecular mass distribution of the hyperbranched
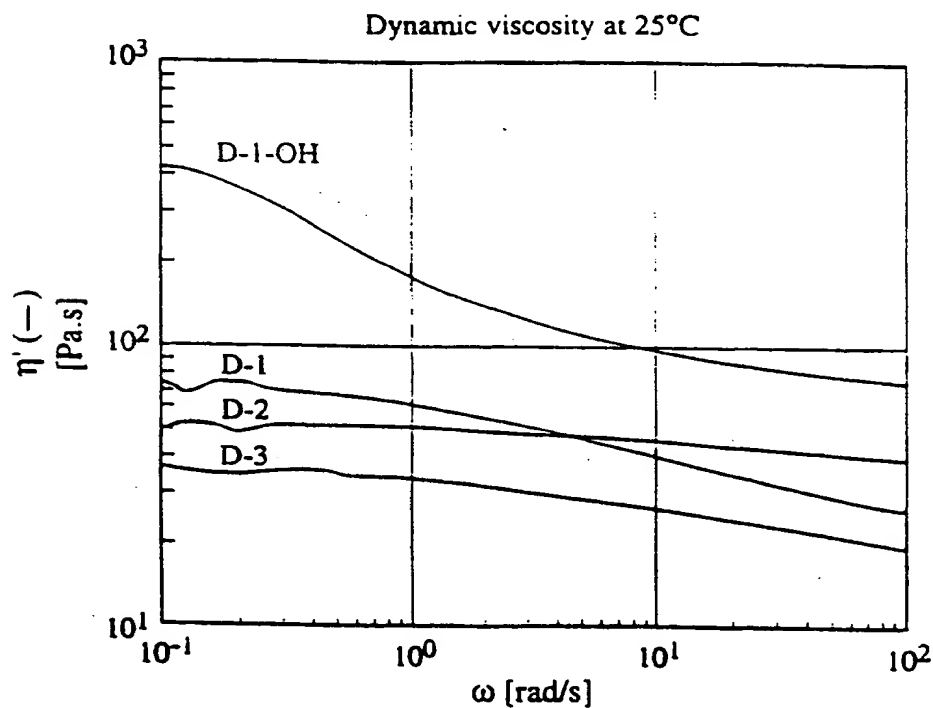methacrylated polyester D-1 analyzed with GPC analysis.



Figure 7   Dynamic viscosity of the hyperbranched
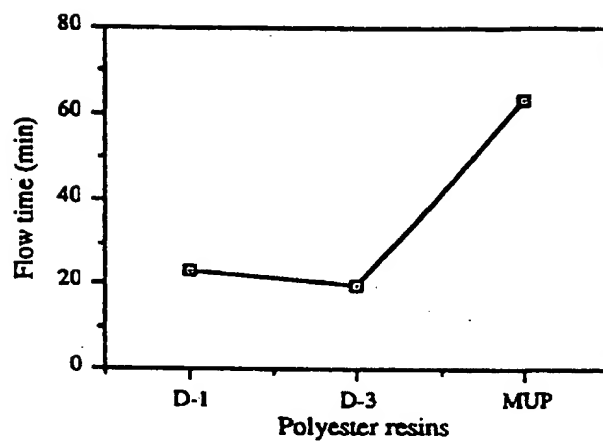(meth)acrylated p lyesters.

**SUBSTITUTE SHEET**

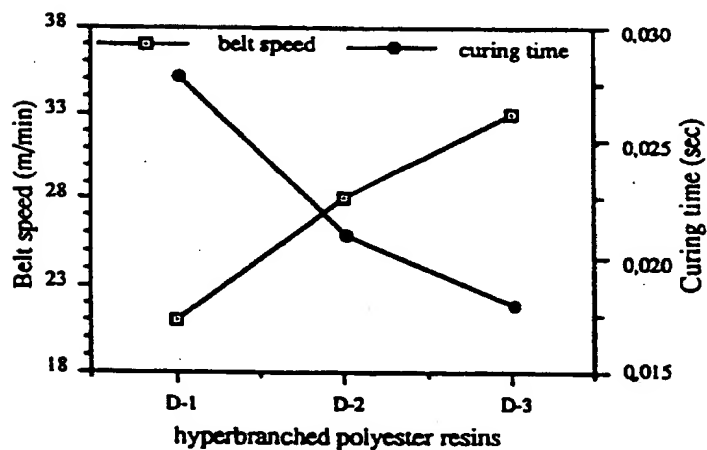Figure 8  Flow time of hyperbranched polyesters and MUP using
viscometric cup



Figure 9  Curing time and belt speed to tack-free state
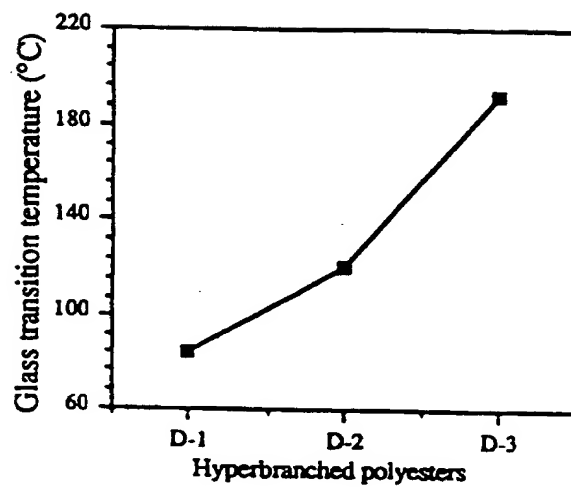for UV cured polyester films

Figure 10  Glass transition temperatures of the cured hyperbranched polyesters.

# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/SE 95/01013**

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC6: C08G 63/20, C08G 63/78, C08J 3/28**
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC6: C08G, C08J**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE,DK,FI,NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**REGISTRY, CAPLUS, WPI, EPODOC**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 9318079 A1 (DSM N.V.), 16 Sept 1993 (16.09.93)<br><br>-- | 1-29 |
| A | WO 9317060 A1 (PERSTORP AB), 2 Sept 1993 (02.09.93)<br><br>--<br>-------- | 1-29 |

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

| | |
|---|---|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| "A" document defining the general state of the art which is not considered to be of particular relevance | |
| "E" erlier document but published on or after the international filing date | "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O" document referring to an oral disclosure, use, exhibition or other means | |
| "P" document published prior to the international filing date but later than the priority date claimed | "&" document member of the same patent family |

| Date of the actual completion of the international search | Date of mailing of th international search report |
|---|---|
| 14 December 1995 | **29 -12- 1995** |
| Name and mailing address of the ISA/<br>**Swedish Patent Office**<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile N . + 46 8 666 02 86 | Authorized officer<br><br>**Sofia Nikolop ulou**<br>Telephone N . + 46 8 782 25 00 |

Form PCT/ISA/210 (second sheet) (July 1992)

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO-A1- 9318079 | 16/09/93 | CN-A- 1076702 | 29/09/93 |
| | | NL-A- 9200416 | 01/10/93 |
| WO-A1- 9317060 | 02/09/93 | AU-A- 3653093 | 13/09/93 |
| | | CA-A- 2117486 | 02/09/93 |
| | | EP-A- 0597042 | 18/05/94 |
| | | EP-A- 0630389 | 28/12/94 |
| | | JP-T- 6507512 | 25/08/94 |
| | | JP-T- 7504219 | 11/05/95 |
| | | SE-B,C- 468771 | 15/03/93 |
| | | SE-A- 9200564 | 15/03/93 |
| | | US-A- 5378886 | 03/01/95 |
| | | US-A- 5418301 | 23/05/95 |